EXTRACTION OF COPPER FROM ITS ORES
The Welsh Copper Process

From "Metals" byC.L. Bloxam sometime Pofesor of Chemistry at King's College, London.
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Probably no other metallurgic operation presents such an appearance of complexity as the smelting of copper ores, but this is due to the great variety of the ores to be treated, which necessitates their introduction at different stages of the process. Thus, a smelting process adapted for copper pyrites must contain provisions for the removal of arsenic and sulphur, which are not present in the carbonates and the oxides of copper, so that the processes of smelting are arranged in such a manner that these ores, as well as the slags obtained in some of the operations, can be introduced after the sulphur and arsenic have been expelled.

In a work like the present, it is not advisable to attempt a detailed account of smelting processes which are subject to frequent alterations in order to suit different lots of ore, particularly when such alterations result from the application of practical experience on the part of the smelter, and do not admit of clear explanation upon simple chemical. principles. A general outline only of the extraction of copper from its ores will be given here, and before this is entered upon, it may assist the reader to state that it may be summed up under the following heads:

1. *Roasting processes,* intended to expel arsenic and sulphur, and to convert the iron into oxide of iron.

2. *Melting processes,* intended to remove the oxide of iron by dissolving it with silica at a high temperature, and to obtain the copper as a pure combination of copper with sulphur (sulphide of copper).

3. *Roasting and melting*, in a single process, to expel the sulphur and obtain metallic copper.

Before being subjected to the first process, the ores are broken into pieces of the size of a nut, and so assorted that the lot to be smelted may contain about eight or ten parts of metallic copper in the hundred. Moreover, as there is much *gangue* or earthy matter associated with the ores, they are, if possible, so mixed that they may serve as *fluxes* to each other, by producing chemical compounds capable of becoming liquefied by the high temperature of the furnace.

The *fluor spar,* which is so commonly associated with copper pyrites, derives its name from its power to effect the liquefaction of earthy substances. Fluor spar is composed of calcium and fluorine; if it be
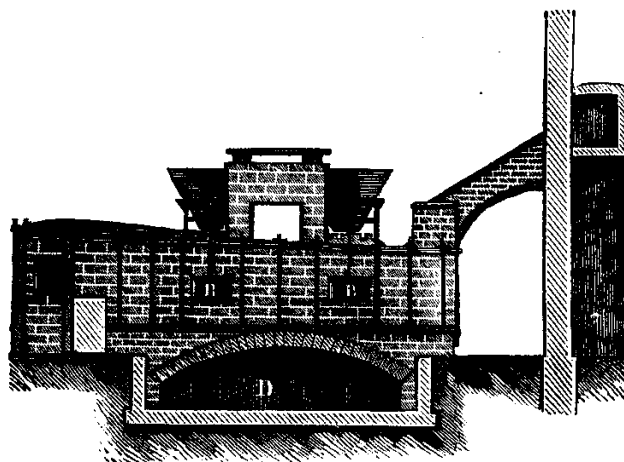

Fig. 55.--Furnace for roasting Copper Ores.
BB, Working doors.
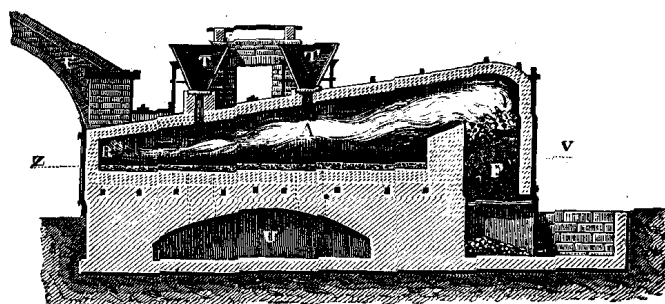v, Vault for receiving the roasted ore.

FIG. 56.--Furnace for roasting Copper Ores.
Section through the line x v of
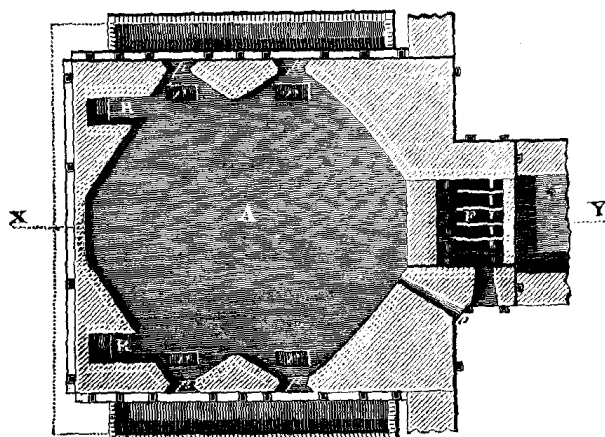the plan (fig. 57).

Fig. 57---Furnace for roasting Copper Ores.
Plan at the line x v of the section (fig. 56}.

strongly heated in contact with silica (quartz), which consists of oxygen combined with silicon, the latter takes up the fluorine to form fluoride of silicon gas, whilst the calcium and oxygen unite to produce lime, which combines with another portion of the silica to form a silicate of lime. The silicate of lime would not easily fuse into a slag by itself, but when clay and oxide of iron are present, as is always the case in the melting furnaces, a slag is readily produced.

1st Process in Copper-smelting. Calcining or Roasting to Expel Arsenic and part of the Sulphur.-- The roasting-furnace or *calciner* (Figs. 55, 56, 57) is a *reverberatory* furnace, with a hearth (A) Of large size (about sixteen feet by fourteen) to allow of the ore being spread out in a thin layer upon it. The hearth is commonly built of fire-bricks set on edge and bedded in fire-clay, and the flame is reverberated upon it by an arch of about two feet in average height. At one end of the hearth, near the fire-place, there is an opening or flue (o) through which air may be admitted to the hearth, to furnish the oxygen necessary for the chemical changes effected in the roasting process. On each side of the hearth there are two openings (r) closed with iron doors, through which the roasted ore is raked out into the arch (u) beneath the furnace. The ore is admitted by opening the hoppers (T) over the arch of the furnace, where it is previously warmed by the waste heat. The fuel employed in the calciners at Swansea is non-caking mixed with one-fourth of bituminous or caking coal, which is necessary to counteract the tendency of the coal to split up into small pieces and fall through the grate unburnt, the bituminous coal being softened by the heat, and binding the free-burning together.

The fire of the calciners requires special management in order that the ore upon the hearth may be brought to the proper temperature. Both the free-burning and caking coal used have had the lumps screened out for household purposes. The small coal would easily fall through the grate. To avoid this, a layer of *clinker* or fused ash from the coal is built up on the bars of the grate (v), preserving them at the same time from direct contact with the glowing coal, and air-passages are made through this layer, so that the air becomes heated in passing through it, before actually reaching the fire, the combustion of the fuel being thus effected by a current of heated air. The oxygen of the air, passing through the column of heated fuel, combines with the carbon to form carbonic oxide, and this gas, being highly heated, takes fire in the air admitted on to the hearth of the furnace, giving a sheet of flame which is drawn through the furnace by the action of the chimney with which the flues (a) communicate, and raises the ore to the temperature necessary for roasting it. Since the air is heavier than the burning gas, a layer of air always exists beneath the latter, separating it from the ore, thus preventing the ore from attaining its melting point, and securing a sufficient supply of oxygen.

Each calciner is charged with three tons of the broken ore, which is spread evenly over the hearth, and roasted for twelve hours, being occasionally raked over through the working-doors (Y) in order to expose fresh portions to the action of the air, and to prevent any part of the ore from being melted. At this high temperature, the arsenic present in the copper ore combines with oxygen from the air to form *arsenious acid* (white arsenic)

which passes, in the form of vapour, into the flues. About half of the sulphur in the ore also combines with oxygen to form *sulphurous acid* gas which passes up the chimney, a small quantity of *sulphuric acid* being also formed and remaining in the ore as sulphate of copper.

Since iron exerts the greater chemical attraction for oxygen, and copper for sulphur, a large proportion of iron acquires oxygen and becomes converted into an *oxide of iron,* while a much smaller proportion of the copper combines with the oxygen from the air to form *suboxide of copper.* When the gases and yapours issuing from the calciners are allowed to escape directly into the air, they form a dense grey cloud of *copper-smoke* which contains the sulphurous acid, mixed with a little yapour of sulphuric acid, the arsenious acid, which condenses in the air to a fine powder, and some hydrofluoric acid gas, produced from the fluor spar. The injurious effect of these products upon the health and vegetation of the neighbourhood has induced the copper smelters to devise means for condensing them by passing them into flues and condensing chambers where they are met by showers of water.

At some works it has been found profitable to convert the sulphurous acid into oil of vitriol instead of allowing it to escape, but in this case it is necessary to prevent the products of combustion of the fuel from mixing with the copper-smoke. *Spence's calciner* employed for this purpose has the fire passing under the hearth instead of over it. This furnace is 50 feet long, and the ore is gradually raked from the cooler to the hotter end as it becomes less fusible. The waste heat of an adjoining smelt!rig furnace is sometimes employed in

these calciners, and the calcined ore is raked at once into the smelting furnace. In *Gerstenhöffer's furnace* the ores are crushed between rollers, and allowed to fall over rows of red hot bricks in a vertical furnace, .through which a blast of heated air is passed in order to burn the sulphur into sulphurous acid, which is then conducted into the leaden chambers, where it is converted into oil of vitriol.

2nd Process in Copper-smelting. Melting for Coarse Metal, to dissolve the Oxide of iron as a Silicate. It has been seen that the 1st process has had the effect of converting a large proportion of the sulphuret of iron present in the pyrites into oxide of iron, which it is the object of the present process to remove by causing it to combine with silica, to form a compound capable of being melted and separated from the rest of the ore. At this stage the copper ores containing silica (quartz) can be introduced with advantage, provided that they are free from sulphur. It must not be forgotten that, during the process of calcining, a small proportion of the sulphuret of copper in the pyrites has been converted into an oxide of copper, which resembles the oxide of iron in its property of combining with silica at a high temperature, to form a melted silicate which would pass away in the slag, entailing a considerable loss of copper. This is prevented by the sulphuret of iron which is still present in the calcined ore, and, at the high temperature at which the fusion is effected, exchanges constituents with the oxide of copper, forming oxide of iron and sulphuret of copper. The slag from the 4th process, to be presently described, is also appropriately introduced in this fusion, since it contains a considerable quantity of oxide of

copper, which exchanges, as above, with the sulphuret of iron in the calcined ore, furnishing more sulphuret of copper to pass into the coarse metal, and oxide of iron to be removed in the slag. The slag from the 4th process (called *metal slag),* being basic, assists in fluxing the silica in the ore. In some cases, the smelter adds some fluor spar in order to facilitate the fusion of the charge.

The *ore-furnace* (Figs. 58, 59), as it is called, in which the melting for coarse metal is effected, is also

FIG. 58.--Section of Ore-furnace for smelting Copper Ores. T, Hopper for introducing the charge. b. Tap-hole for discharging the slag into the slag-moulds u. c, Flue leading to the chimney.

Fig,. 59.--Plan of Ore-furnace for smelting Copper Ores.   r, The grate.

a reverberatory furnace, but its hearth (k) is much smaller than that of the calciner (usually about one-third of the size), because the charge has to be raised to a much higher temperature; for which reason, also, the fire-grate is larger in proportion; the hearth is also slightly inclined on all sides towards a depression or cavity (B) at one side, which serves as a crucible in which the melted coarse-metal collects. The fuel is a mixture of free-burning with one-third of bituminous coal. The charge of this furnace is composed of the following materials, selected for the
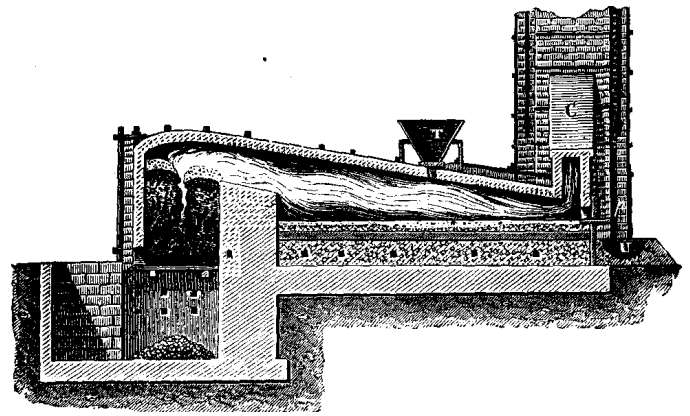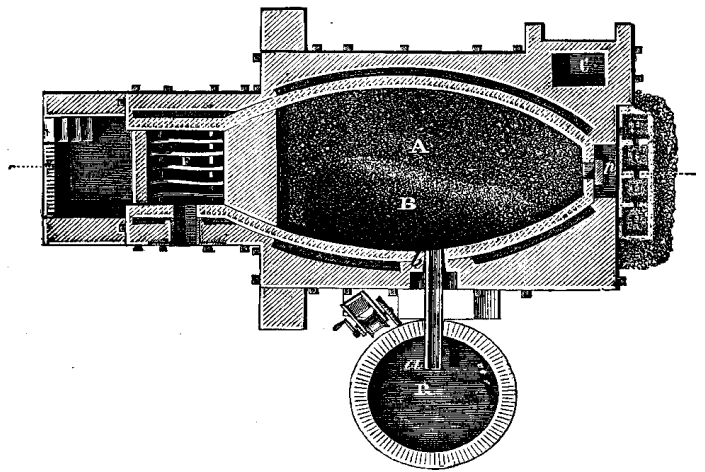
reasons above given, viz. :-

Calcined or roasted ore, usually about x8 cwt. Ores containing oxide of copper and silica, 3 cwt.

Metal-slag from process 4, containing oxide of iron, silica, and some oxide of copper, 6 cwt.

Fluor-spar, occasionally.

The slag is the first to fuse, in about half-an-hour after the charge has been introduced, and by degrees the whole of the materials become liquid, and enter into violent ebullition, caused by disengagement of sulphurous acid gas, produced by a secondary decomposition of no importance from a metallurgic point

of view, save that the ebullition favours the intimate mixture of the melted matters on the hearth.

After three or four hours, the furnace-man mixes up the melted matters with a rake, and raises the temperature very considerably, to favour the separation of the coarse metal from the slag. In about half-an-hour, the tap-hole (b, Fig.59), which communicates with the cavity in the hearth, is opened, and the *matte* or *regulus* of coarse metal is run out, through an iron gutter (a) into an iron box (G, Fig. 6o), perforated at the bottom and standing in a cistern through which water is constantly running; the coarse metal is thus *granulated* or divided into small irregular grains, in order to fit it for undergoing the next operation.

Sometimes the regulus from two or three operations is allowed to accumulate in the furnace before tapping, the slag alone being raked out before the introduction of a fresh charge. The iron box containing the regulus is raised from out of the cistern by a winch (w),
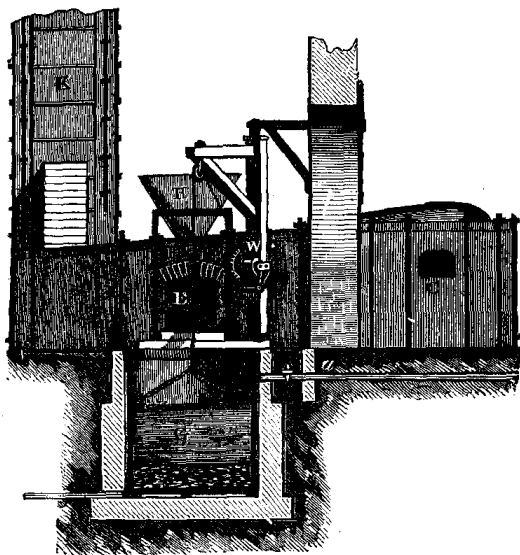
and its contents are carried to the calcining furnace.

This coarse metal contains copper, iron, and sulphur in .about the same proportion in which they are present in pure copper pyrites, so that the copper amounts to about 33 parts in the hundred, or nearly four times the proportion contained in the raw ore at the commencement of the process.

The slag *(ore-furnace slag)* is raked out into sand-moulds (v, Fig. 59), connected with each other by openings in their sides, where it solidifies into blocks of a black, somewhat glassy, appearance, interspersed with white fragments of quartz. It is used for rough building purposes in the neighbourhood of the copper works.. The ore-furnace slag is composed essentially of oxide of iron (ferrous oxide) and silica combined in about equal proportions, and would be 'spoken of. in chemical language, as a *silicate of iron* or *ferrous silicate.* It contains also a little copper, usually amounting to one part in x4o parts, representing a loss to the smelter which appears unavoidable. Occasionally, a small quantity of regulus is found at the bottom of the

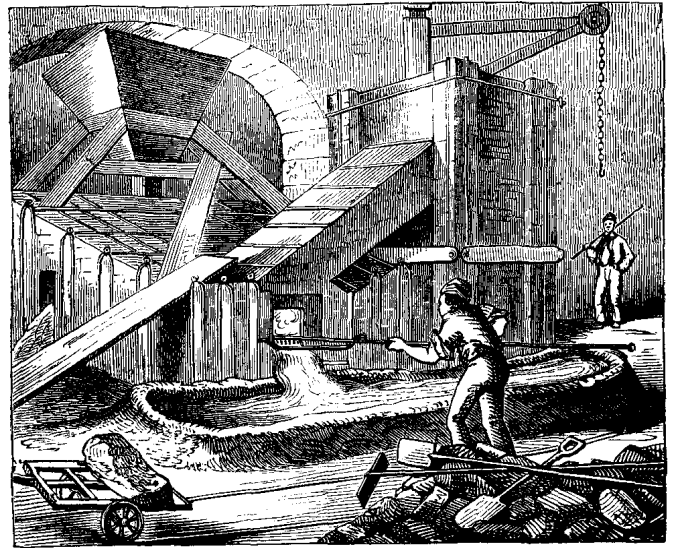
Fig. 61.– Copper Smelting-Furnace

blocks of slag, from which it is separated by hand-picking. Fig. 61r exhibits the general arrangements connected with the ore-furnace, and shows the furnace-man discharging the slag.

3rd -Process in Coiltier-smelting. Calcination of the Coarse Metal, to convert more of the Sulphuret of Iron into Oxide.--Now that the earthy matter has been removed in the slag, it is far easier to oxidise the sulphuret of iron than it was in the first calcining process. To effect this, three tons of the granulated coarse metal are roasted in the calcining furnace (Fig.. 57) for 24 hours, the temperature being moderated at the commencement, to avoid fusion, and gradually raised in proportion as the removal of the sulphur diminishes the fusibility of the charge, which is raked over every two hours. About one-half of the sulphur is converted by the oxygen of the air into sulphurous and sulphuric acids, which escape in vapour, another portion of oxygen combining with the iron from which the sulphur has been removed, to form oxide of iron, so that the roasted coarse metal consists essentially of sulphuret of copper, oxide of iron, and some unchanged

Fig. 6o.--Elevation of Ore-furnace for smelting Copper Ores. u, Hopper for introducing the charge. K, Chimney.   c~ Fire-door. a~ Pipe for supplying water to the tank.

sulphuret of iron.

4th Process in Copper- smelting. Fusion of the Calcined Coarse Metal lo remove all the iron and to obtain Fine Metal.--The principles involved in this process are the same as in the second process.

The fusion is effected in a furnace which does not differ materially from that employed in the 2rid process, except that there is no cavity in the hearth, which is made to slope from all parts towards the tap-hole (Fig. 59). The charge consists of-

Calcined coarse metal (about one ton)

Roaster-slag from the 5th process
Refinery-slag from the 6th process
Ores containing oxide and carbonate of copper
About 12. cwt

(The roaster and refinery slags contain silica in combination with the oxides of iron and copper)

These materials are fused together for about six hours, when they divide, as before, into a regulus or matt, and a slag,. which remains above it. This regulus is called *fine metal.,* to distinguish it from the *coarse metal* of the 2rid process; it may contain from 60 to 80 per cent. of copper, according to the amount of oxidised products and ores containing oxide and carbonate of copper added to the melting-charge. The different qualities are distinguished by specific terms; thus, when the metal contains from 6o to 7o per cent. of copper and has a smooth shining fracture and blue colour, it is called *blue metal;* from 75 to 78 per cent., the fracture is granular, the lustre greasy, and the colour greyish-white, it is then called *white metal;* when the percentage of copper is above 78, the surface of the metal is covered

with pimples, and *moss* copper is found in the air cavities, it is then called *pimple metal.* The pimples are formed by escaping sulphurous acid gas.

When it is intended to manufacture *best selected copper* for making brass, gun-metal, &c., the fine metal is made to undergo a partial roasting; the various impurities which are present tend to collect in the metallic copper, which is thus .separated from the melted mass of regulus. Two or more roastings may be required. The metallic copper containing the impurities is termed bottoms. The unreduced fine metal ,or *regule,* which should now be nearly free from impurities, is treated in the ordinary way for copper. If gold, silver, tin, lead, iron, nickel, manganese, antimony, or arsenic be present in only small traces, they can, without difficulty, be .entirely eliminated by the above selecting process.

The composition of a sample of these bottoms is here given, in 100 parts: copper 74, tin 14, antimony 4½, lead 1, iron 2½ sulphur 4. It is evident that the metallic copper which has separated has decomposed the sulphurets of tin, .antimony, &c. contained in the metal, and has combined with those metals to form an alloy, which is heavier than the metal and sinks to the bottom.

In some smelting-works, where the fine metal is not obtained in so pure a condition, and contains only 60 parts of copper in the hundred, it is again submitted to the two processes of calcining and melting, exactly as in processes 3 and 4, when it yields *black copper* or *coarse copper,* which contains from 70 to 80 parts of copper in the hundred.

The *metal-slag,* as the slag from the 4th process is termed, presents

an appearance very different from that of the ore-furnace slag; it is very crystalline and lustrous, and consists chiefly of oxide of iron combined with silica, but it contains a considerable proportion of copper, partly in the form of an oxide in combination with silica, and partly as small particles of metallic copper, disseminated through the mass. In some specimens of the metal-slag, the copper appears in very fine brilliant filaments, forming *copper-moss.* This slag is usually employed as part of the charge in the 2nd process {melting for coarse metal).

5th Process in Copper-smelting. Calcining or Roasting the Fine Metal to remove Sulphur and obtain Blister- Copper.-The manner in which this process is carried out is varied according to the degree of purity of the fine metal, but the chemical principles which it involves are the following: When a compound of copper with sulphur is heated in air, the sulphur combines with the oxygen of the air, and is thus gradually removed in the form of sulphurous acid gas, the copper also combining with oxygen, and being left as oxide of copper. Further, when an oxide of copper (or compound of copper with oxygen) is melted in contact with a sulphuret of copper (or compound of copper with sulphur), the oxygen of the former combines with the sulphur of the latter to form sulphurous acid gas, and the copper is separated in the metallic state.

The pigs of blue metal are introduced, to the amount of 1½ ton, into a reverberatory furnace, where they are roasted, at a gradually increasing temperature so as to avoid fusion, for about four hours, in order that a part of the sulphuret of copper may be converted into oxide of copper.

When it is judged that this has been effected to a proper extent, the temperature is further raised so as to fuse the materials upon the hearth, the doors of the furnace being closed in order to avoid excess of air. As soon as the mass is fairly liquefied, the temperature is somewhat reduced, being again raised towards the close. During this fusion a violent effervescence is observed in the liquid mass, due to the escape of sulphurous acid gas, formed by the union of the sulphur from the sulphuret with the oxygen from the oxide of copper, whilst metallic copper subsides, in a fused state, and is run out into sand-moulds, where it solidifies into ingots, which preserve a blistered appearance, caused by the escape of sulphurous acid during solidification. The duration of the process depends upon the degree of purity of the blue metal under treatment, but it varies between 12 and 24 hours.

A small quantity of slag (called *roaster-slag*) is formed during the fusion, which resembles pumice in its porous texture, but has a dark red-brown colour, and consists of the oxides of iron and copper combined with silica derived partly from the hearth of the furnace, and partly from the sand-moulds in which the ingots of blue metal are cast. This slag contains about 16 parts of copper in a hundred, and is used as a portion of the charge in the 4th process.

The roasting-furnace employed in this process is often constructed with an air-channel (Fig. 62)traversing the whole length of the fire-bridge, open to the air at both ends, and communicating with the hearth of the furnace through two openings (b b) in the brickwork. This permits the introduction of heated air into the hearth, by which the roasting is much facilitated.

6th Process of Copper-smelting. Refining and Toughening, to purify the Copper.-- The pigs of blister-copper are far from pure; they contain considerable proportions of sulphur, arsenic, iron, tin, lead and other foreign substances, varying according to the descriptions of ore employed. In order to remove these impurities, the oxygen of atmospheric air is brought into use. The furnace employed does not differ very materially from the melting-furnace used in the 2nd process (Fig. 58). The blister-copper to be refined is piled, in charges of 6 or 8 tons, upon the hearth, in such a manner as to allow air to circulate freely among the ingots. A moderate heat is applied at first, to allow the oxygen of the air to act upon the blister-copper, an action which is facilitated by the porous structure of the metal. The sulphur then becomes converted into sulphurous acid gas, and the arsenic into arsenious acid, which passes off in vapour, whilst the iron, tin, lead and other foreign metals are converted into oxides, as well as a portion of the copper. After being roasted for about six hours, the metal is melted, when a thin layer of slag is formed upon its surface; after raking this off, a large sample of the copper is withdrawn and examined by the refiner, who can judge from the appearance of its surface if the oxidation has proceeded to the necessary extent. In order to toughen the metal, its surface is covered with wood-charcoal or anthracite, which is renewed from time to time, so as to shield the copper from further oxidation, and
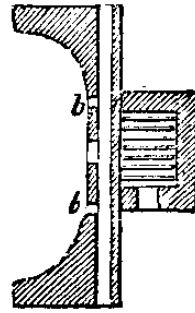

FIG. 62.

the melted metal is stirred with a pole of young wood (usually birch), until a small sample half cut through with a chisel and then broken exhibits a fine close grain, a silky fracture, and a light-red colour, and a small ingot, cast for the purpose and hammered when red-hot, is found to be soft and free from cracks at the edges. The copper is then said to be at *tough-pitch,* and is taken out in iron ladles lined with clay, and cast into ingots of *tough-cake* copper.

The effect of this process of *poling,* as it is termed, in toughening the copper, depends upon the removal of oxygen from the metal. When the blister-copper has been refined, as above described, by being very slowly melted in contact with air, it is found to have taken up a large proportion of oxygen, which is contained dissolved in the metal as an oxide *(suboxide)* of copper. The presence of the oxygen, though it does not amount to more than two or three parts in a thousand of copper, has the effect of rendering the copper brittle or *dry,* so that a small ingot of it is easily broken when hammered, and its fracture exhibits a deep red colour, and a coarse-gained, somewhat crystalline structure. When the pole is plunged beneath the melted metal the combustible gases, generated from the wood by the heat, effect the removal of the oxygen from the metal, and bring it by degrees to tough-pitch. If, during the operation of casting the ingots, the surface of the metal on the hearth be not well covered with charcoal or anthracite the copper will go *back* or become brittle again, in consequence of the absorption of oxygen from the air.

If the process of poling be continued after the copper has been brought to tough-pitch, it becomes even more brittle than before it was

poled, an effect which was formerly ascribed to the combination of the copper with a little carbon from the wood; but since analysis has failed to prove the presence of the carbon, the following less simple explanation, based upon experiment, is now generally received. Perfectly pure copper exhibits the malleability and ductility of the metal in the highest perfection, but these qualities are deteriorated by the presence of small proportions of the various foreign matters, such as sulphur, tin, antimony, &c., which cannot be entirely removed in the refining process. The injurious effect of these impurities, however, is counteracted in some measure by the presence of a small proportion .of oxygen (not exceeding two parts in a thousand), so that if this element be entirely removed, the copper will be *over-poled,* exhibiting a brittle character, due to some of the above-named impurities. On the other hand, if too much oxygen has been left in the metal, the copper is dry or *underpoled.* The effect of overpoling upon the metal may be remedied by .allowing air to act for a short time upon the melted copper, :so that a small quantity of oxygen may be absorbed by it.

When the copper is intended for rolling into sheets, it is usual to add lead, in the proportion of about five parts to a thousand of copper, just before skimming the surface in order to ladle out the copper. The metal is well stirred after the addition of lead, in order that the action of the air may produce an oxide of lead, which combines with the oxides of tin, antimony, and other foreign metals, to form a liquid slag, which rises to the surface of the metal and is skimmed off before casting. It is necessary that the removal of the lead from the copper by oxidation should be as complete as possible,

since its presence would prevent the scale of oxide of copper from being easily detached from the sheet during the process of rolling, and even 1/10 th part of lead in 100 parts of copper suffices to injure its quality.

This treatment of the metal with lead is called *scorification,* from the *scoria* or slag which forms upon the surface.

The *refinery slag,* skimmed from the surface of the melted .copper before commencing the process of paling, has a dull brown-red colour, with a purple shade, and consists almost entirely of an oxide of copper (suboxide) combined with silica derived from the hearth and from the sand-moulds employed to cast the blistered copper. It is employed in the 4th process (fusion for fine metal).

The hearths of the copper-furnaces become strongly impregnated with copper in course of time, and are broken out in order that the metal may be removed from them.

The following modified method has been found to work successfully, By calcination or mixture a 28 per cent. coarse metal is produced. With this percentage a cleaner slag is obtained than with a 35 per cent.; a 35 per cent. has, however, the advantage of calcining better in the subsequent operation. In order to obtain this latter advantage as well as a clean slag, the 28 per cent. metal is melted down with the requisite amount of roaster and refinery slag, thus enriching the metal to the required extent. This method has the additional advantage that the roaster and refinery slags being introduced at an earlier stage than in the ordinary process, the impurities have a greater chance of being eliminated.

This 19th century text has been scanned in and there could be some scanning errors. The chemistry may not be as we would describe it.